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AUTHORITY

afrpl ltr, 28 mar 1979

AFRPL-TR-68-40 AGC 1082-81Q-6

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

H. Moe and A. J. Di Milo
Chemical and Physical Sciences Section
Aerojet-General Corporation
Sacramento, California

Quarterly Technical Report AFRPL-TR-68-40

February 1968

Sponsored by

Air Force Rocket Propulsion Laboratory
Research and Technology Division
Edwards, California
Air Force Systems Command, United States Air Force

AFRPL-TR-68-40

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

H. Moe and A. J. Di Milo

FOREWORD

This technical report was prepared under Contract No. AF 04(611)-11637 as partial fulfillment of the requirements of Project No. 3148 of the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California. The work was performed in the Chemical and Physical Sciences Section of the Research and Technology Department, Aerojet-General Corporation, Sacramento, California. This report was designated Aerojet-General Report 1082-81Q-6 and covers the progress made in the period 1 November to 31 January 1968. This project was monitored by Lt. Robert Bargmeyer, 1/Lt., USAF/RPCS.

J. T. Becerril, Senior Laboratory Technician has contributed materially to the work performed during this period at Aerojet-General Corporation.

Prepared by:

A. J. Di Milo
Program Manager

H. Moe
Principal Investigator

Approved by:

L. J. Rosen, Manager
Solid Propellant Research Group
Research & Technology Department

Publication of this report does not conetitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

Chemical studies of the composition of binder in aged propellants was continued. Model urethane and urea were stable over 2 weeks in contact with various combinations of NH_4ClO_4, aluminum, ferric acetylacetonate, and copper chromite. Aging sites from a Polaris Cycling Unit have been separated from the aluminum and NH_4ClO_4 which are embedded within them. Analysis of this material has been delayed because of its insolubility in the common laboratory solvents. As the material may be a crosslinked polymer, further degradation may have to precede the analysis.

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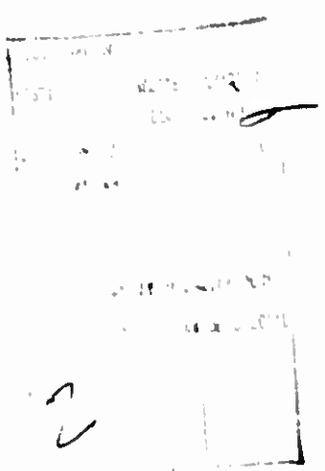

AFRPL-TR-68-40

MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

I. INTRODUCTION

This is the sixth Quarterly Technical Report submitted in partial fulfillment of the requirements of Contract AF 04(611)-11637. The report covers the period 1 November to 31 January 1968.

The objectives of this study are to determine the course of the chemical aging process or processes in solid propellant formulations and to define the effects of these degradative chemical processes on the mechanical and ballistic properties of the propellant.

In accordance with these general objectives, the studies have been divided into two phases. The objectives in Phase I are to determine the structure, size and distribution of microscopic reaction sites in solid propellants as a function of age, formulation and storage environments; and to optically characterize and chemically analyze the reaction intermediates and products. In Phase II the mechanistic course of the aging process will be defined.

Work during the sixth quarter consisted of chemical studies of aged propellants.

II. CHEMICAL STUDIES

Work reported in the last quarterly, Report AFRPL-TR-67-289, described experiments which established that plasticizer (IDP) migration across a bipropellant interface occurred to a significant degree and that this plasticizer was the liquid vehicle for the migration of iron acetylacetonate (FeAA). The ultimate fate of the FeAA was dependent upon whether aluminum was available for chemical reaction. Where available, Al reduced the iron in FeAA from the ferric to the ferrous state. In the absence of Al, the FeAA remained stable, even after ambient storage of the propellant for up to 6 years. The mobility of FeAA and the oxidation-reduction between Al and FeAA might lead to side effects, such as influencing the chemical stability of the binder or of compounds derived from the binder which are susceptible to oxidation-reduction. Further oxidation-reduction of the binder would lead to lower propellant stability. To determine whether the above considerations affect propellant stability, aging studies on model compounds were made.

The stability of a model urethane and a model urea in contact with NH_4ClO_4, NH_4ClO_4 and Al, NH_4ClO_4, Al and FeAA, and NH_4ClO_4, Al, FeAA, and copper chromite was studied. Two solutions of dimethoxyethane (glyme) containing ethyl carbanilate (10 wt%) and dimethylurea (10 wt%) were prepared

and 0.5-g aliquots were separately mixed with about equal weights of the four solid propellant combinations. The mixtures were sealed in glass vials and stored at 50°C. At intervals, the concentration of ethyl carbanilate and of dimethylurea was determined by gas chromatography. A 2-ft column packed with 60-80 mesh Diatoport-S coated with 10 wt% of silicone green rubber SE30 was used and a programmed heating rate of 15°C/min between 75-200°C allowed separation of the model compound from the phenylcyclohexane internal standard. Analyses showed that even after 14 days at 50°C, both the urethane and the urea remained intact in all environments. This would indicate that chemical reaction between FeAA and Al did not lead to chemical reactions of the functional groups of a polyurethane binder.

These experiments are not definitive with respect to the time element, because the interval of study was short compared with the age of many of the propellants studied (3 to 6 years). On the other hand, study of some model propellant grains had indicated that aging site formation occurred after about 2 weeks storage.

There is another factor which may be important in this respect. The aluminum is normally coated with oxide and in this form is relatively unreactive. From studies made at Aerojet several years ago, Dr. A. E. Oberth concluded that during propellant mixing the aluminum oxide coating was scratched clean. He postulated the reaction of this clean surface with glycols formed aluminum alkoxides and indicated that this was the cause of "soft-center" cures. In a further study Dr. R. Olberg showed that the soluble aluminum (alkoxide form) increased with length of mixing, solids content, and type of glycol. This explanation must, therefore, be accepted as highly probable.

While neither of these workers considered the effect of these reactions on the stability of the binder, this consideration is important because a highly reactive specie such as aluminum alkoxide could affect the stability of binders. It is also pertinent because acid-terminated prepolymers such as PBAA, PBAN, and CTPBD should also react readily with a clean aluminum surface. Presently, however, an effective experimental attack on this problem has not been formulated. The chemical study of the urethane or urea stability in the presence of propellant solid ingredients indicates only the effect of the oxide-coated aluminum.

III. MICROSCOPIC STUDIES

A. REACTION SITE MATERIAL

A more extensive examination was made of the composition of the reaction sites from an aged Polaris Cycling Unit. Because of the relatively low total concentration of these reaction sites, earlier efforts to investigate this material were hampered by lack of material. The isolation technique was improved and the supply of reaction site material for further study has

increased. The degraded propellant was mixed with ethylene dichloride as previously to dissolve out the low molecular weight binder fragments, leaving a mixture of NH_4ClO_4, Al and the reaction site clusters as a slurry. The ethylene dichloride was decanted and the slurry was treated with dimethyl formamide, which dissolved the NH_4ClO_4, leaving only Al and the reaction site clusters. The mixture was passed through a screen of appropriate mesh to separate the smaller Al from the reaction site clusters. Figures 1a to d show, respectively; (a) a typical reaction site in a thin section of propellant from a degraded zone; (b) four reaction sites isolated by ethylene dichloride, and contaminated with some NH_4ClO_4; (c) a reaction site leached with dimethylformamide to remove NH_4ClO_4; (d) a fragmented particle which originally was part of a reaction site cluster.

Efforts were made to analyze the composition of the material shown in Figure 1d. This clear material was insoluble in hot polar solvents as dimethylformamide, dimethyl sulfoxide and water, as well as common organic solvents. It was yellow-green, isotropic, non-birefringement and amorphous, with a refractive index of 1.53 ± 0.02. At the present time, it appears that this material is a high molecular weight, crosslinked polymer. Attempts are being made to convert it into a soluble form for analysis.

B. POSSIBLE TRANSFORMATION OF NH_4ClO_4 IN AGED PROPELLANT

Based upon some earlier observations, it was tentatively suggested that one of the effects of propellant aging was the conversion of NH_4ClO_4 into NH_4Cl. Such a conversion, if confirmed, would have significant effects on the ballistic performance of such propellants. An attempt was therefore made to establish whether any NH_4Cl could be found in degraded propellant from the Polaris Cycling Unit.

Five grams of propellant from the degraded zone were extracted with hot water and several drops of the aqueous extract were allowed to evaporate. Microscopic examination of the crystalline residue revealed it to be NH_4ClO_4, with no evidence of any other salts being present. In a calibration test, it was found that the presence of 1.00 wt% NH_4Cl in NH_4ClO_4 could be easily detected by this method. An aqueous solution was prepared from 1.000 g NH_4ClO_4 and 0.010 g NH_4Cl and a few drops allowed to evaporate. Two distinct types of crystals formed; NH_4ClO_4, orthorhombic and anisotropic and NH_4Cl, dendritic and isotropic. Other differences were that NH_4ClO_4 dissolved in dimethylformamide, while NH_4Cl did not. In addition, the refractive index of NH_4ClO_4 (1.48) could be easily distinguished from that for NH_4Cl (1.64).

PHOTOMICROGRAPHS OF THE SEPARATION OF NH_4ClO_4 AND ALUMINUM FROM REACTION SITE FROM POLARIS CYCLING UNIT

a

b

c X250

d X1000

Figure 1

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)
Aerojet-General Corporation
P. O. Box 15847
Sacramento, California

2a. REPORT SECURITY CLASSIFICATION
None

2b. GROUP

3. REPORT TITLE
MICROSCOPIC AND MICROCHEMICAL STUDY OF AGED SOLID PROPELLANT GRAINS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)
Sixth Quarterly Report - 1 November to 31 January 1968

5. AUTHOR(S) (First name, middle initial, last name)
Di Milo, Anthony J.
Moe, Henry

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
February 1968	9	None

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 04(611)-11637	1082-81Q-6
b. PROJECT NO. 3148	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

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11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Air Force Rocket Propulsion Laboratory
Research and Technology Operations
Edwards, California
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United States Air Force

13. ABSTRACT

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DD FORM 1 NOV 65 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Grain Aging						
Propellant Aging						
Microscopic Techniquee						
Hawk Aging						
Polyurethane Aging						
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